

PATENT SPECIFICATION

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(54) DETERGENT

(71) We, COLGATE-PALMOLIVE COMPANY, a Corporation organised and existing under the Laws of the State of Delaware, United States of America, of 300 Park Avenue, New York, New York 10022, United States of America, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

This invention relates to detergents.

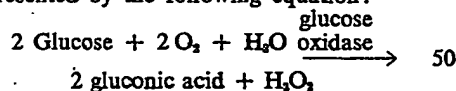
According to the invention a detergent composition comprises a detergent material selected from organic surface active agents, builder salts and mixtures thereof; glucose and glucose oxidase, or starch, amyloglucosidase and glucose oxidase, as a hydrogen peroxide precursor; and a hydroxylamine, defined as hydroxylamine free base or a hydroxylamine salt.

Preferably the detergent composition comprises a detergent material selected from organic surface active agents, builder salts and mixtures thereof; a hydrogen peroxide precursor selected from (A) 5 to 30% by weight of glucose, and 0.5 to 10% by weight of glucose oxidase and (B) 5 to 30% by weight of starch, 0.5 to 10% by weight of amyloglucosidase and 0.5 to 10% of glucose oxidase; and 0.5 to 5% by weight of hydroxylamine; the composition having pH of 5 to 7.5 upon dilution in water at a concentration of 0.2 to 1% by weight. Except where otherwise indicated, percentages by weight are based on the composition.

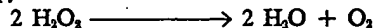
The detergent is prepared in solid form generally as a powder, and in use is dissolved in water in the presence of oxygen or air.

Glucose and glucose-oxidase enzyme, or starch, amyloglucosidase enzyme which hydrolyzes starch to glucose and glucose-oxidase enzyme are employed to form hydrogen peroxide in water during washing.

The glucose-glucose oxidase reaction is represented by the following equation:



In this equation starch and amyloglucosidase may replace glucose. Glucose oxidase has a potency of 1300 to 1500 units per gram measured in accordance with the procedure in the Journal of Agricultural and Food Chemistry, 1953, page 1727. Glucose oxidase typically is an impure enzyme and is mixed with catalase, an enzyme effective upon hydrogen peroxide to decompose immediately the peroxide to water and oxygen in accordance with the following equation:



Therefore, in order to permit glucose and glucose oxidase, or starch, amyloglucosidase and glucose oxidase, to be used to form hydrogen peroxide effective for bleaching purposes, it is also necessary to prevent catalase breakdown of hydrogen peroxide.

The present invention is based on the discovery that a hydroxylamine, i.e. hydroxylamine free base or salts of hydroxylamine such as hydroxylamine sulphate, hydroxylamine nitrate, hydroxylamine fluosilicate and hydroxylamine halides including hydroxylamine chloride and hydroxylamine bromide, prevent the breakdown of hydrogen peroxide by catalase and are compatible with other components of the detergent composition. Thus, by employing a hydroxylamine in the composition, glucose and glucose oxidase can form hydrogen peroxide in water and the peroxide formed is present during washing and is highly effective at the moment of bleach. The preferred hydroxylamine is hydroxylamine sulphate.

The surface active agent may be any commonly used compound having surface active properties. Most preferred are those water-

soluble surface active compounds having anionic or nonionic properties. Anionic surface active agents contain an organic hydrophobic group and an anionic solubilizing group. Typical examples of anionic solubilizing groups are sulphonate, sulphate, carboxylate, and phosphate. Examples of suitable anionic detergents are soaps, such as water-soluble salts of higher fatty acids or rosin acids, which may be derived from fats, oils and waxes of animal, vegetable or marine origin, e.g. sodium soaps of tallow, grease, coconut oil, tall oil and mixtures thereof; and sulphated and sulphonated synthetic detergents, particularly those having 8 to 26, preferably 12 to 22, carbon atoms to the molecule.

Examples of suitable synthetic anionic detergents are higher alkyl mononuclear aromatic sulphonates such as higher alkyl benzene sulphonates containing from 10 to 16 carbon atoms in the alkyl group in a straight or branched chain, e.g. sodium salts of decyl, undecyl, dodecyl (lauryl), tridecyl, tetradecyl, pentadecyl or hexadecyl benzene sulphonate and higher alkyl toluene, xylene and phenol sulphonates; alkyl naphthalene sulphonate, ammonium diamyl naphthalene sulphonate and sodium dinonyl naphthalene sulphonate; sulphated aliphatic alcohols such as sodium lauryl and hexadecyl sulphates, triethanolamine lauryl sulphate and sodium oleyl sulphate; sulphated alcohol ethers, such as lauryl, tridecyl, or tetradecyl sulphates including 2-4 ethylene oxide moieties; sulphated and sulphonated fatty oils, acids or esters, such as sodium salts of sulphonated castor oil and sulphated red oil; sulphated hydroxy-amides such as sulphated hydroxyethyl lauramide; sodium salt of lauryl sulphoacetate; sodium salt of dioctyl sulphosuccinate; and sodium salt of oleyl methyl tauride.

Other anionic surface active agents which may be employed are olefin sulphonates, typically containing 8 to 25 carbon atoms.

Other examples are sulphuric acid esters of polyhydric alcohols incompletely esterified with higher fatty acids, e.g. coconut oil monoglyceride monosulphate and tallow diglyceride monosulphate; and hydroxy sulphonated higher fatty acid esters such as higher fatty acid esters of low molecular weight alkylol sulphonic acid, e.g. oleic acid ester of isethionic acid.

Nonionic surface active agents contain an organic hydrophobic group and a hydrophilic group which is a reaction product of a solubilizing group such as carboxylate, hydroxyl, amido or amino with ethylene oxide or with the polyhydration product thereof, polyethylene glycol.

Examples of nonionic surface active agents are condensation products of alkyl phenols with ethylene oxide, e.g. the reac-

tion product of isooctyl phenol with 6 to 30 ethylene oxide units; condensation products of alkyl thiophenols with 10 to 15 ethylene oxide units; condensation products of higher fatty alcohols such as tridecyl alcohol with up to 50 ethylene oxide units; ethylene oxide addends of monoesters of hexahydric alcohols and inner ethers thereof such as sorbitan monolaurate, sorbitol mono-oleate and mannitan monopalmitate, and the condensation products of polypropylene glycol with ethylene oxide.

Cationic surface active agents may also be employed. These contain an organic hydrophobic group and a cationic solubilizing group. Typical cationic solubilizing groups are amine and quaternary groups.

Examples of suitable synthetic cationic detergents are diamines such as those of the type $RNHC_2H_4NH_2$, wherein R is an alkyl group of 12 to 22 carbon atoms such as N-aminoethyl stearyl amine and N-aminoethyl myristyl amine; amide-linked amines such as those of the type $R'CONHC_2H_4NH_2$, wherein R' is an alkyl group of 12 to 18 carbon atoms, such as N-amino ethyl-stearyl amide and N-amino ethyl myristyl amide; quaternary ammonium compounds wherein typically one of the groups linked to the nitrogen atom is an alkyl group of 12 to 18 carbon atoms and three of the groups linked to the nitrogen atom are alkyl groups which contain 1 to 3 carbon atoms, including such 1 to 3 carbon alkyl groups bearing inert substituents, such as phenyl groups, and there is present an anion such as halogen, acetate or methosulphate. Typical quaternary ammonium detergents are ethyl-dimethyl-stearyl ammonium chloride, benzyl-dimethyl-stearyl ammonium chloride, trimethyl-stearyl ammonium chloride, trimethyl-cetyl ammonium bromide, dimethyl-ethyl lauryl ammonium chloride, dimethyl-propyl-myristyl ammonium chloride, and the corresponding methosulphates and acetates.

The surface active compounds which are used in the most preferred forms of this invention are those having anionic properties. The most highly preferred water-soluble anionic detergents are ammonium and substituted ammonium (such as mono, di- and triethanolamine), alkali metal (such as sodium and potassium) and alkaline earth metal (such as calcium and magnesium) salts of higher alkyl benzene sulphonates, higher alkyl sulphates and higher fatty acid monoglyceride sulphates.

The builder which may be employed may be any water-soluble inorganic builder salt commonly known in the art, or it may be a water-soluble organic sequestering agent such as sodium nitrilotriacetate, or mixtures thereof.

The water-soluble inorganic builder salts may be alkali metal, alkaline earth metal or

heavy metal salts, or combinations thereof. An ammonium or an ethanol-ammonium salt may be used, but generally the sodium and potassium salts are preferred. Examples are the water-soluble sodium and potassium phosphates, silicates, carbonates, bicarbonates, borates, sulphates and chlorides. Particularly preferred builder salts are the alkaline builder salts such as polyphosphates, silicates and borates.

In water-soluble inorganic builder salt mixtures it is often preferred to have present a mixture of sodium tripolyphosphate and sodium or potassium bicarbonate, such as a combination of salts wherein the bicarbonate to tripolyphosphate ratio is in the range 1:1 to 3:1, by weight.

Both Phase I and Phase II sodium tripolyphosphate, and mixtures thereof, may be used. The usual commercial tripolyphosphate consists mainly of the Phase II material. The commercial tripolyphosphate material is usually essentially tripolyphosphate, e.g. 87 to 95%, with small amounts, e.g. 4 to 13% of other phosphates, e.g. pyrophosphate and orthophosphate. Sodium tripolyphosphate in its hydrated form may be used also. Trisodium orthophosphate may also be used.

The sodium or potassium bicarbonate is an effective pH buffer. The bicarbonate may be incorporated directly as anhydrous bicarbonate or in the form of sesquicarbonate, a hydrate containing both bicarbonate and carbonate.

The detergent material may be present in amount of 5 to 94% by weight. Typically, when a mixture of organic surface active agent and builder salt is employed, the composition contains 10 to 25% by weight of 25% by weight of the surface active agent and 45 to 74% by weight of the builder.

The composition preferably contains 15 to 30% by weight of glucose or starch; 2.5 to 5% by weight of amyloglucosidase when starch is used; 2.5 to 5% by weight of glucose oxidase; and 1 to 3% by weight of the hydroxylamine.

As already indicated, it is desirable that upon dilution in water at typical used concentrations, i.e. 0.2 to 1% by weight of the composition in water, that the solution be from lightly acid to weakly basic, that is in pH range of 5 to 7.5. As the pH gets more strongly basic than 7.5, the activity of the enzyme is decreased.

The composition may also contain additives such as carboxymethylcellulose or polyvinylpyrrolidone. These additives may be present in amount of 0.1 to 5% by weight. The composition may also optical brighteners, perfumes and preservatives. Activators such as N-benzoyl succinimide may also be present.

The composition may be prepared by add-

ing glucose, glucose oxidase and hydroxylamine salt, or starch, amyloglucosidase, glucose oxidase and hydroxylamine salt, to the detergent material. Typically, the detergent material is first prepared by spray drying. If hydroxylamine free base is employed, it is preferably added to the detergent material before spray drying. The preparation may also be prepared by dry blending.

In use, the detergent preparation may be dissolved in water in a washing machine, such as a drum or agitator washing machine, in amount of 2 grams to 10 grams, preferably 5 grams, per litre of water to provide a solution having a lightly acid or weakly basic pH of 5 to 7.5. The action of the washing machine provides sufficient contact with air and water to form hydrogen peroxide from glucose and glucose oxidase or from starch, amyloglucosidase and glucose oxidase during washing. The formation of hydrogen peroxide is not adversely affected at temperatures ranging from ambient temperature to 55°C. During washing the temperature may then be raised to effect bleaching.

The following examples illustrate the invention. All amounts are by weight unless otherwise specified.

Example I

The following composition was prepared:

	Percent
Glucose oxidase	10
Glucose	20
Hydroxylamine sulphate	1.5
Na ₂ HPO ₄ - KH ₂ PO ₄ mixture	to 100

The theoretical maximum H₂O₂ concentration which could be obtained with this composition is 3.55×10^{-3} m/l at 25°C. 120 grams of the composition was dissolved in 24 litres of water, resulting in a pH of 5.8, and agitated in the presence of air. The concentration of hydrogen peroxide after various periods of time was determined as follows:

Time in Minutes	Concentration H ₂ O ₂
10	1×10^{-3} m/l
20	1.7×10^{-3} m/l
30	2.3×10^{-3} m/l
40	2.8×10^{-3} m/l
60	3.5×10^{-3} m/l

Thus, effective amounts, up to almost 100% of the theoretical amount, of hydrogen peroxide were formed, and decomposition of hydrogen peroxide was inhibited by the presence of the hydroxylamine salt. Similar results were obtained when the glucose was replaced by 20% starch and 10% amyloglucosidase and the amount of phosphate mixture reduced accordingly.

Example II

The effect of pH on the amount of hydrogen peroxide which is formed from the glucose-glucose oxidase formulation of Example I, in solution in water in the pre-

sence of air and upon agitation at 25°C, was determined.

The amount of hydrogen peroxide formed after 60 minutes at various pH values is indicated below:

	pH	% hydrogen peroxide in relation to theory
	5	—
	5.8	99
10	7	72
	7.5	—
	8	32
	9	22

Thus, at lightly acid to weakly basic pH values between 5 and 7.5 there was desirable formation of hydrogen peroxide without an undesirable amount of decomposition into water and oxygen. Similar results were obtained with the starch-amyloglucosidase formulation.

Example III

The following compositions were prepared:

	Parts	
	A	B
25 Sodium tallow soap	10	10
C ₁₆ -C ₁₈ Fatty alcohol condensate with 23 moles of ethylene oxide	7	7
30 Ethylene diamine tetra-acetic acid, tetra sodium salt	0.2	0.2
Sodium tripolyphosphate	35.0	35.0
35 Sodium sulphate	qs to 100	qs. to 100
Glucose	20	
Glucose oxidase	10	
Hydroxylamine sulphate	2	

In the test described below, 3.2×10^{-3} moles of hydrogen peroxide per litre of solution were added to composition A. Each composition also contained sulphuric acid in sufficient amount to obtain a pH of 7 upon dilution in water.

45 Composition B was dissolved in cold water (20°C) in an agitator washing machine at a dilution of 5 g/l. Fabric squares tinted with Immedial black were immersed in the solution (IMMEDIAL is a trade mark).
50 Composition B remained in cold water for 50 minutes during which time 3.2×10^{-3} m/l of hydrogen peroxide were formed which corresponds to the amount of hydrogen peroxide in Composition A. The temperature
55 was then raised to the boil. Composition A was used shortly after the addition of hydrogen peroxide. It was dissolved in water at the same concentration as composition B and the temperature was raised to the boil
60 in an agitator washing machine. Fabric squares tinted with Immedial black were also immersed in this solution.

The efficacy of bleaching of the fabric squares with composition B in which hydrogen peroxide was formed from glucose and

glucose oxidase in the presence of the hydroxylamine salt was compared with that of composition A which contained freshly added hydrogen peroxide. The efficacy of bleaching was determined as the increase in reflectance of the fabric squares (Δ).

After two tests with preparation B, Δ was found to be 7 and 7. After two tests with preparation A, Δ was found to be 7.65 and 7.85.

Thus, the preparation in which hydrogen peroxide was formed from glucose and glucose oxidase and prevented from decomposing by the hydroxylamine salt was practically equivalent in bleaching efficacy to a preparation which contained freshly added hydrogen peroxide.

Similar effective bleaching was obtained when hydroxylamine free base, hydroxylamine chloride, hydroxylamine nitrate and hydroxylamine fluosilicate were substituted for hydroxylamine sulphate in composition B, and when 20% starch and 10% amyloglucosidase were substituted for glucose in composition B (the amount of sodium sulphate being reduced accordingly).

Furthermore, similar effective bleaching was obtained when composition B was modified by replacing the condensate of C₁₆-C₁₈ fatty alcohol with 23 moles of ethylene oxide with a condensate of C₁₄-C₁₆ fatty alcohol with 50 moles of ethylene oxide, and when the nonionic surface active agent was omitted altogether.

Example IV

The following detergent composition was prepared:

	Parts	
Sodium tallow soap	6	
Sodium dodecyl benzene sulphonate	3	105
C ₁₆ -C ₁₈ Fatty alcohol condensate with 50 moles of ethylene oxide	6	
Sodium carboxymethyl cellulose	0.8	
Ethylene diamine tetraacetic acid, tetrasodium salt	0.14	110
Sodium tripolyphosphate	35.0	
Brighteners and perfume	0.413	
Glucose	20	
Glucose oxidase	5	
Hydroxylamine sulphate	1.6	115
Sodium sulphate and impurities	qs to 100	

This composition was permitted to remain in water adjusted at pH 7 with sulphuric acid, at 40°C at a dilution of 5 g/l. The moles of hydrogen peroxide per millilitre formed after various periods were determined to be: 23 minutes = 0.31×10^{-6} ; 31 minutes = 0.48×10^{-6} ; 38 minutes = 0.73×10^{-6} ; 45 minutes = 0.94×10^{-6} ; 56 minutes = 1.16×10^{-6} . This desirable and effective formation of hydrogen peroxide was stabilized against catalase decomposition by the hydroxylamine.

WHAT WE CLAIM IS:—

1. A detergent composition comprising a

detergent material selected from organic surface active agents, builder salts and mixtures thereof; glucose and glucose oxidase, or starch, amyloglucosidase and glucose oxidase, as a hydrogen peroxide precursor; and hydroxylamine as hereinbefore defined.

2. A detergent composition comprising a detergent material selected from organic surface active agents, builder salts and mixtures thereof; a hydrogen peroxide precursor selected from (A) 5 to 30% by weight of glucose and 0.5 to 10% by weight of glucose oxidase, and (B) 5 to 30% by weight of starch, 0.5 to 10% by weight of amyloglucosidase and 0.5 to 10% by weight of glucose oxidase; and 0.5 to 5% by weight of hydroxylamine as hereinbefore defined; the composition having a pH of 5 to 7.5 upon dilution in water at a concentration of 0.2 to 1% by weight.

3. A detergent composition as claimed in Claim 2 wherein the glucose is present in amount of 15 to 30% by weight, the glucose oxidase is present in amount of 2.5 to 5% by weight and the hydroxylamine is present in amount of 1 to 3% by weight.

4. A detergent composition as claimed in

Claim 2 wherein the starch is present in amount of 15 to 30% by weight, the amyloglucosidase is present in amount of 2.5 to 5% by weight, the glucose oxidase is present in amount of 2.5 to 5% by weight and the hydroxylamine is present in amount of 1 to 3% by weight.

5. A detergent composition as claimed in any of the preceding claims wherein the hydroxylamine is hydroxylamine base.

6. A detergent composition as claimed in any of Claims 1 to 4 wherein the hydroxylamine is a hydroxylamine salt.

7. A detergent composition as claimed in Claim 6 wherein the hydroxylamine salt is hydroxylamine sulphate, hydroxylamine nitrate, hydroxylamine fluosilicate or hydroxylamine halide.

8. A detergent composition as claimed in any of the preceding claims wherein the detergent material comprises an organic synthetic anionic surface active agent.

9. A detergent composition substantially as described in any of the Examples.

KILBURN & STRODE,
Chartered Patent Agents,
Agents for the Applicants.